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(54) **MULTIPLE CATALYST SYSTEM AND POLYMERIZATION PROCESS FOR USE THEREOF**

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(60) Provisional application No. 62/012,047, filed on Jun. 13, 2014.

(51) **Int. Cl.**

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C08F 4/613	(2006.01)
C08F 4/6592	(2006.01)
C08F 210/16	(2006.01)
C08F 4/602	(2006.01)
C08F 4/659	(2006.01)

(52) **U.S. Cl.**

CPC ***C08F 210/16*** (2013.01); ***C08F 4/6022*** (2013.01); ***C08F 4/6028*** (2013.01); ***C08F 4/69*** (2013.01); *C08F 4/65912* (2013.01); *C08F 4/6925* (2013.01)

(58) **Field of Classification Search**

CPC C08F 4/69; C08F 4/6592; C08F 4/65912; C08F 210/16; C08F 4/6022

See application file for complete search history.

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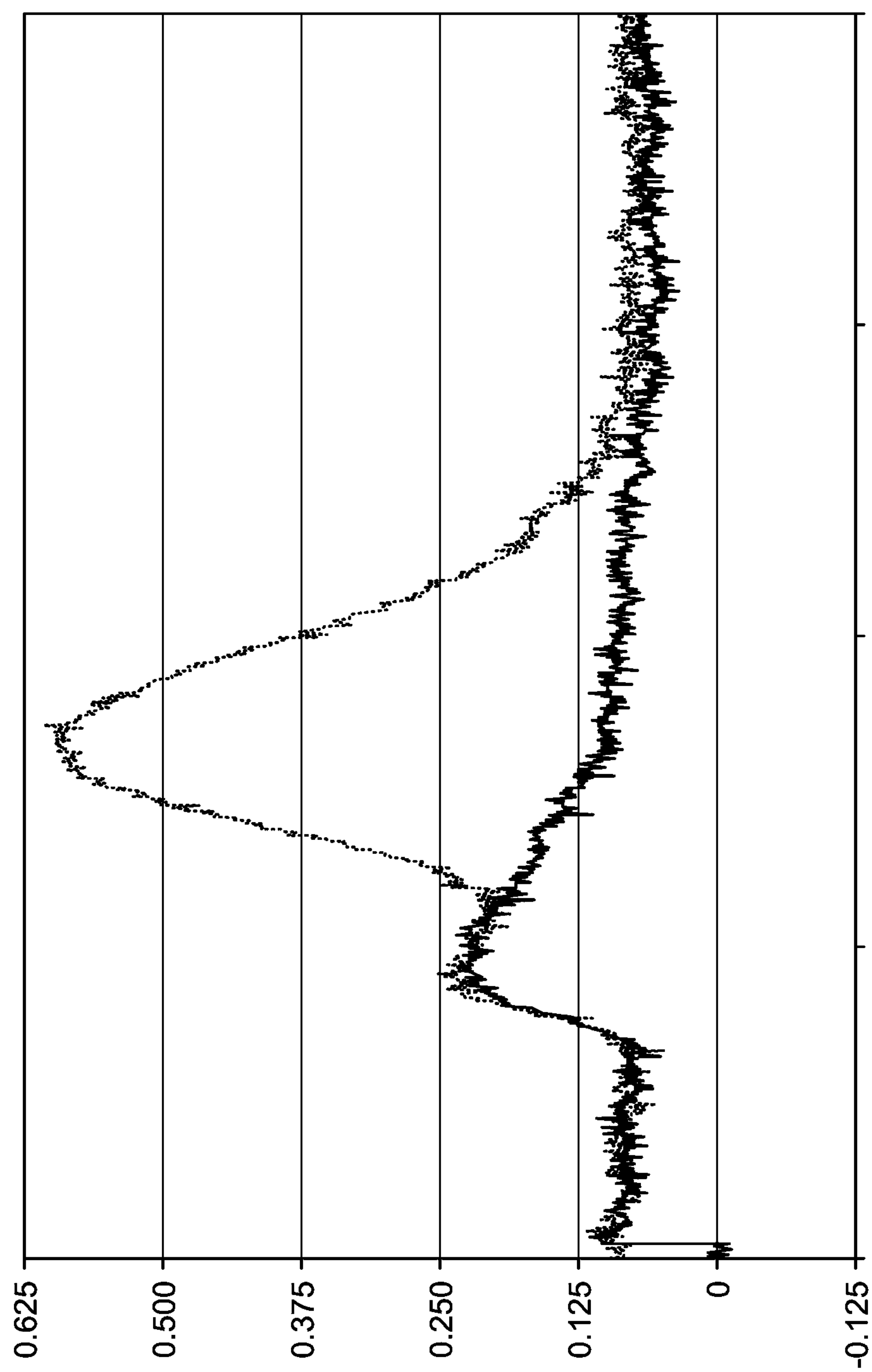
Primary Examiner — Caixia Lu

(57) **ABSTRACT**

This invention relates to a catalyst system comprising a half sandwich chromocene compound featuring a tethered N-donor, with an alumoxane and consequent supportation on silica produces a catalyst that produces ultra-high molecular weight polyethylene and that further supportation of a catalyst capable of producing linear low density polyethylene produces a multiple-catalyst system on the same support, capable of producing polyethylene with a bimodal molecular weight distribution and excellent molecular weight.

25 Claims, 1 Drawing Sheet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0.500
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MULTIPLE CATALYST SYSTEM AND POLYMERIZATION PROCESS FOR USE THEREOF

PRIORITY

This application is a continuation of U.S. Ser. No. 14/723,607, filed May 28, 2015, which claims priority to and the benefit of U.S. Ser. No. 62/012,047, filed Jun. 13, 2014.

FIELD OF THE INVENTION

This invention relates to catalyst systems comprising two metallocene catalyst compounds, one a group 4 metal compound and the other a chromium compound, and their use to polymerize olefins.

BACKGROUND OF THE INVENTION

It is thought that adding an ultra-high molecular weight component to polyethylene resins of lower molecular weight may improve the properties of that resin (melt strength, stiffness, etc.) and simultaneously retain the processing properties normally associated with the lower molecular weight PE. However, simple blending of ultra-high molecular weight polyethylene and a linear low density polyethylene may result in both melt and solid phase separation. (See Chen, Y.; Zou, H.; Liang, M.; Liu, P. *J. App. Polym. Sci.* 2013, 129, 945-953.) Producing an ultra-high molecular weight polyethylene in the same reactor as a lower molecular weight material may be a cost-effective way of creating a bimodal resin with the two molecular weight components already intimately mixed. Thus, if a catalyst capable of producing ultra-high molecular weight polyethylene could be cosupported with a metallocene catalyst such that the two catalysts did not interfere with one another, it is thought that such a resin could be produced in a very straightforward and economical manner. However, selecting catalyst combinations that are compatible (i.e., do not interfere with each others' ability to produce polymer) and produce desired product is a challenge.

Half sandwich chromocenes are disclosed in DE 19710615; WO 2012/040147; US 2013/225820; US 2010/267901; CN 102070732. In particular, *J. Organometallics* 2000, 19, 388-402 (Dohring, A. et al.) discloses ethylene (cyclopentadienyl) (pyrrolidine)chromium dichloride.

Further, WO 2006/052232 discloses a catalyst comprising a chromocene and bis(n-butyl cyclopentadienyl)zirconium dichloride to produce broad Mw/Mn, high molecular weight polyethylene.

WO 2011/089017 discloses the preparation of high molecular weight polyethylene using a catalyst of a half sandwich indenyl chromocene and a hafnocene.

WO 2008/140175 discloses a combination of metallocene with chromium catalyst on the same support.

Other references of interest include: US 2012/059134, and *Macromol. Rapid Comm.,* 2010, 31, 1359-1363 (d. Kurek, A, et al.).

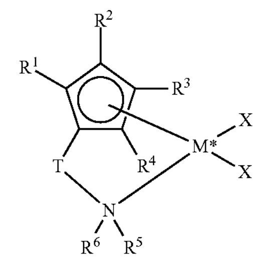
There is still a need in the art for new and improved catalyst systems for the polymerization of olefins, in order to achieve specific polymer properties, such as impact resistance without negatively impacting the resulting polymer's processability properties.

It is therefore an object of the present invention to provide novel catalyst compounds, catalyst systems comprising such compounds, and processes for the polymerization of olefins using such compounds and systems. Accordingly, it has been discovered that activation of a half sandwich chromocene compound featuring a tethered N-donor, with an alumoxane and consequent supportation on silica produces a catalyst that produces ultra-high molecular weight polyethylene and that further supportation of a catalyst capable of producing linear low density polyethylene produces a 2-catalyst system on the same support, capable of producing polyethylene with a bimodal molecular weight distribution, excellent molecular weight, and good activity.

SUMMARY OF THE INVENTION

This invention relates to a catalyst system comprising activator, support, catalyst compound represented by Formula I and catalyst compound represented by Formula II, and a process to polymerize olefins (such as ethylene) with said catalyst system, where:

Formula I is



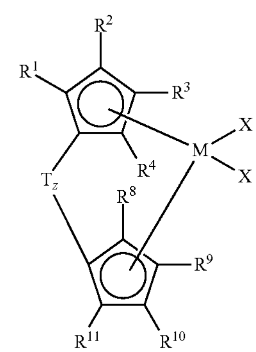
where

T is a bridging group; N is nitrogen; M* is Cr, Mo, or W, where M* is in a +3 oxidation state prior to contacting with activator; each X, is independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides and C_1 to C_5 alkyl groups, preferably each X is a chloride, bromide or a methyl group;

each R^1, R^2, R^3, and R^4 is independently, hydrogen, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group; and

each R^5 and R^6 is, independently, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group, where the R^5 and R^6 groups may form a fused ring or multicenter fused ring system where the rings may be aromatic, partially saturated or saturated; and

Formula II is:



where

M is Hf or Zr; T is a bridging group; z is 0 or 1;

each X, is independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides and C_1 to C_5 alkyl groups, preferably each X is a chloride, bromide or a methyl group; and

each R^1, R^2, R^3, R^4, R^8, R^9, R^{10}, and R^{11} is, independently, hydrogen, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group.

This invention relates to a method to polymerize olefins comprising contacting a supported catalyst with an activator and one or more monomer. This invention further relates to novel catalyst systems. This invention further relates to polymer compositions produced by the methods described herein.

BRIEF DESCRIPTION OF THE FIGURES

FIG. **1** is a GPC trace for PE-6 from the examples with the GPC trace for PE-3 overlaid.

DETAILED DESCRIPTION

For the purposes of this invention and the claims thereto, the new numbering scheme for the Periodic Table Groups is used as described in Chemical and Engineering News, 63(5), pg. 27 (1985).

An "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an "ethylene" content of 35 wt % to 55 wt %, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt % to 55 wt %, based upon the weight of the copolymer. A "polymer" has two or more of the same or different mer units. A "homopolymer" is a polymer having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other. "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An "ethylene polymer" or "ethylene copolymer" is a polymer or copolymer comprising at least 50 mole % ethylene derived units, a "propylene polymer" or "propylene copolymer" is a polymer or copolymer comprising at least 50 mole % propylene derived units, and so on.

Preferably the terms "polyethylene" and "ethylene polymer" mean a polyolefin comprising at least 50 mol % ethylene units and having less than 15 mol % propylene units. Preferably, the "polyethylene" and "ethylene polymer" comprise at least 60 mol %, preferably, at least 70 mol %, preferably, at least 80 mol %, even preferably, at least 90 mol %, even preferably, at least 95 mol % or preferably, 100 mole % ethylene units; and have less than 15 mol % propylene units. Thus, while ethylene-rich ethylene-propylene copolymers are generically a class of ethylene copolymer, a special distinction is made herein for the composition range commonly associated with EP Rubber, as defined below. The comonomers in an ethylene copolymer, if present, are preferably chosen from C_3 to C_{20} olefins (preferably C_3 to C_8 1-olefins). An "ethylene elastomer" is an ethylene copolymer having a density of less than 0.86 g/cm^3. An "ethylene plastomer" (or simply a "plastomer") is an ethylene copolymer having a density of 0.86 to 0.91 g/cm^3. A "low density polyethylene" is an ethylene polymer having a density of more than 0.91 g/cm^3 to less than 0.94 g/cm^3; this class of polyethylene includes copolymers made using a heterogeneous catalysis process (often identified as linear low density polyethylene, LLDPE) and homopolymers or copolymers made using a high-pressure/free radical process (often identified as LDPE). A "high density polyethylene" ("HDPE") is an ethylene polymer having a density of 0.94 g/cm^3 or more. Density is typically determined according to ASTM D1505.

The term "EP Rubber" means a copolymer of ethylene and propylene, and, optionally, one or more diene monomer(s), where the ethylene content is from 35 to 85 mol %, the total diene content is 0 to 5 mol %, and the balance is propylene with a minimum propylene content of 15 mol %; and where the copolymer has a Mooney viscosity, ML(1+4) @ 125° C. (measured according to ASTM D1646) of 15 to 100.

For the purposes of this invention, ethylene shall be considered an α-olefin.

For purposes of this invention and claims thereto, the term "substituted" means that a hydrogen group has been replaced with a heteroatom, or a heteroatom containing group. For example, a "substituted hydrocarbyl" is a radical made of carbon and hydrogen where at least one hydrogen is replaced by a heteroatom or heteroatom containing group.

As used herein, Mn is number average molecular weight, Mw is weight average molecular weight, and Mz is z average molecular weight, wt % is weight percent, and mol % is mole percent. Molecular weight distribution (MWD), also referred to as polydispersity, is defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (e.g., Mw, Mn, Mz) are g/mol. The following abbreviations may be used herein: Me is methyl, Et is ethyl, Pr is propyl, cPR is cyclopropyl, nPr is n-propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, sBu is sec-butyl, tBu is tert-butyl, Oct is octyl, Ph is phenyl, Bn is benzyl, MAO is methylalumoxane.

A "catalyst system" is combination of at least one chromium metallocene catalyst compound (represented by Formula I), at least one group 4 metal metallocene compound (represented by Formula II), at least one activator, an optional co-activator, and at least one support material. For the purposes of this invention and the claims thereto, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers.

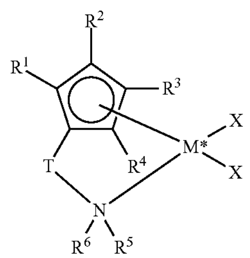
In the description herein, the metallocene catalyst may be described as a catalyst precursor, a pre-catalyst compound, metallocene catalyst compound or a transition metal compound, and these terms are used interchangeably. A polymerization catalyst system is a catalyst system that can polymerize monomers to polymer. An "anionic ligand" is a negatively charged ligand which donates one or more pairs of electrons to a metal ion. A "cationic ligand" is a positively charged ligand which donates one or more pairs of electrons to a metal ion. A "neutral donor ligand" is a neutrally charged ligand which donates one or more pairs of electrons to a metal ion.

A metallocene catalyst is defined as an organometallic compound with at least one π-bound cyclopentadienyl moiety (or substituted cyclopentadienyl moiety) and more frequently two π-bound cyclopentadienyl moieties or substituted cyclopentadienyl moieties.

For purposes of this invention and claims thereto in relation to metallocene catalyst compounds, the term "substituted" means that a hydrogen group has been replaced with a hydrocarbyl group, a heteroatom, or a heteroatom containing group. For example, methyl cyclopentadiene (Cp) is a Cp group substituted with a methyl group.

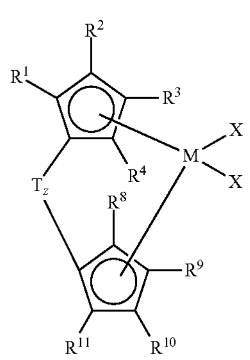
Catalyst System

In a preferred embodiment, this invention relates to catalyst systems comprising activator(s), support(s), at least one catalyst compound represented by Formula I and at least one catalyst compound represented by Formula II, where Formula I is



where T is a bridging group; N is nitrogen; M* is Cr, Mo, or W, preferably Cr, where M* is in a +3 oxidation state prior to contacting with activator; each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides and C_1 to C_5 alkyl groups, preferably each X is a chloride, bromide or a methyl group; each R^1, R^2, R^3, and R^4 is, independently, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group; and each R^5 and R^6 is, independently, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group, where the R^5 and R^6 groups may form a fused ring or multicenter fused ring system where the rings may be aromatic, partially saturated or saturated; and

Formula II is:



where M is Hf or Zr, preferably Zr; T is a bridging group; z is 0 or 1; each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides and C_1 to C_5 alkyl groups, preferably each X is a chloride, bromide or a methyl group; and each R^1, R^2, R^3, R^4, R^8, R^9, R^{10}, and R^{11} is, independently, hydrogen, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group.

In a preferred embodiment of the invention in any embodiment of any formula described herein, each R^1, R^2, R^3, R^4, R^8, R^9, R^{10}, and R^{11} is, independently, hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, docecyl, or an isomer thereof, Cl, Br, F, I, or Si, preferably methyl, ethyl, propyl, butyl or an isomer thereof.

In a preferred embodiment of the invention, each R^5 and R^6, is, independently, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, docecyl, or an isomer thereof, Cl, Br, F, I, or Si.

In a preferred embodiment of the invention in any embodiment of any formula described herein, the R^5 and R^6 groups form a 3 to 24 membered fused ring with the nitrogen atom, where the rings may be aromatic, partially saturated or saturated, preferably saturated. In an embodiment, the ring (s) have 3 to 20, alternately 4 to 18, alternately 5 to 15, alternately 6 to 12. Useful $N(R^5)(R^6)$ fragments include: pyrrolidine, aziridine, azetidine, piperidine, azepane, azocane, azonane, azecane, 1H-azirine, 1,2-dihydroazete, 2-pyrroline, 3-pyrroline, 1,4-dihydropyridine, azepine, azonine, indole, isoindole, indoline, isoindoline, or substituted versions thereof, where the substituents are alkyl, aryl, silyl, and or halide groups.

Useful $N(R^5)(R^6)$ fragments are neutral donor ligands. A neutral donor ligand is defined as one that, in its uncoordinated state, bears a formal charge of zero. Useful $N(R^1)(R^2)$ fragments are not anionic ligands and are not cationic ligands.

In a preferred embodiment of the invention in any embodiment of any formula described herein, T is a bridging group and is represented by R'_2C, R'_2Si, R'_2Ge, $R'_2CCR'_2$, $R'_2CCR'_2CR'_2$, $R'_2CCR'_2CR'_2CR'_2$, $R'C{=}CR'$, $R'C{=}CR'CR'_2$, $R'_2CCR'{=}CR'CR'_2$, $R'C{=}CR'CR'{=}CR'$, $R'C{=}CR'CR'_2CR'_2$, $R'_2CSiR'_2$, $R'_2SiSiR'_2$, $R_2CSiR'_2CR'_2$, $R'_2SiCR'_2SiR'_2$, $R'C{=}CR'SiR'_2$, $R'_2CGeR'_2$, $R'_2GeGeR'_2$, $R'_2CGeR'_2CR'_2$, $R'_2GeCR'_2GeR'_2$, $R'_2SiGeR'_2$, $R'C{=}CR'GeR'_2$, $R'B$, $R'_2C{-}BR'$, $R'_2C{-}BR'{-}CR'_2$, $R'_2C{-}O{-}CR'_2$, $R'_2CR'_2C{-}O{-}CR'_2CR'_2$, $R'_2C{-}O{-}CR'_2CR'_2$, $R'_2C{-}O{-}CR'{=}CR'$, $R'_2C{-}S{-}CR'_2$, $R'_2CR'_2C{-}S{-}CR'_2CR'_2$, $R'_2C{-}S{-}CR'_2CR'_2$, $R'_2C{-}S{-}CR'{=}CR'$, $R'_2C{-}Se{-}CR'_2$, $R'_2CR'_2C{-}Se{-}CR'_2CR'_2$, $R'_2C{-}Se{-}CR_2CR'_2$, $R'_2C{-}Se{-}CR'{=}CR'$, $R'_2C{-}N{=}CR'$, $R'_2C{-}NR'{-}CR'_2$, $R'_2C{-}NR'{-}CR'_2CR'_2$, $R'_2C{-}NR'{-}CR'{=}CR'$, $R'_2CR'_2C{-}NR'{-}CR'_2CR'_2$, $R'_2C{-}P{=}CR'$, or $R'_2C{-}PR'{-}CR'_2$ where each R' is, independently, hydrogen or a C_1 to C_{20} containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl substituent and optionally two or more adjacent R' may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent. Preferably, T is a bridging group comprising carbon or silica, such as dialkylsilyl, preferably T is selected from CH_2, CH_2CH_2, $C(CH_3)_2$, $SiMe_2$, $SiPh_2$, SiMePh, silylcyclobutyl ($Si(CH_2)_3$), $(Ph)_2C$, $(p-(Et)_3SiPh)_2C$, and cyclopentasilylene ($Si(CH_2)_4$).

In a preferred embodiment of the invention in any embodiment of any formula described herein, T is represented by the formula $R_2{}^aJ$, where J is C, Si, or Ge, and each R^a is, independently, hydrogen, halogen, C_1 to C_{20} hydrocarbyl or a C_1 to C_{20} substituted hydrocarbyl, and two R^a can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system.

In a preferred embodiment of the invention in any embodiment of any formula described herein, T is represented by the formula, $(R^*{}_2G)_g$, where each G is C, Si, or Ge, g is 1 or 2, and each R* is, independently, hydrogen, halogen, C_1 to C_{20} hydrocarbyl or a C_1 to C_{20} substituted hydrocarbyl, and two or more R* can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system, preferably T is CH_2, CH_2CH_2, $C(CH_3)_2$, $SiMe_2$, $SiPh_2$, SiMePh, $Si(CH_2)_3$, $Si(CH_2)_4$, $Si(CH_2)_5$, or CPh_2.

In an embodiment of the invention in any embodiment of any formula described herein, M is Cr and M* is Hf.

In an embodiment of the invention in any embodiment of any formula described herein, M is Cr and M* is Zr.

In a preferred embodiment of the invention in any embodiment of any formula described herein, R_1 and R_8 are Me, R_3 and R_{10} are n-butyl.

In a preferred embodiment of the invention in any embodiment of any formula described herein, R_1 and R_8 are Me, R_3, z is 0, and R_{10} are n-butyl.

The transition metal compounds may be used in any ratio. Preferred molar ratios of metal in (A) transition metal compound(s) represented by Formula I to metal in (B) transition metal compound(s) represented by Formula II (i.e., the molar ratio of M* to M) fall within the range of (A:B) 1:1000 to 1000:1, alternatively 1:100 to 500:1, alternatively 1:10 to 200:1, alternatively 1:1 to 100:1, and alternatively 1:1 to 75:1, and alternatively 5:1 to 50:1. The particular ratio chosen will depend on the exact compounds chosen, the method of activation, and the end product desired. In a particular embodiment, when using the two catalyst compounds, where both are activated with the same activator, useful mole percents, based upon the molecular weight of the catalyst compounds, are 10 to 99.9% A to 0.1 to 90% B, alternatively 25 to 99% A to 0.5 to 50% B, alternatively 50 to 99% A to 1 to 25% B, and alternatively 75 to 99% A to 1 to 10% B.

In a preferred embodiment of the invention, the molar ratio of the metal in the compound(s) represented by Formula I to the metal in the compound(s) represented by Formula II is from 0.1:1 to 100:1, preferably from 0.25:1 to 75:1, preferably from 0.25:1 to 50:1, preferably from 0.5:1 to 30:1, preferably from 0.75:1 to 20:1, preferably from 0.8:1 to 10:1, preferably from 0.8:1 to 5:1, preferably from 0.8:1 to 2:1. In an embodiment, the molar ratio of the metal in the compound(s) represented by Formula I to the metal in the compound(s) represented by Formula II is 5:6.

In a preferred embodiment of the invention, the Cr to Zr molar ratio for the catalyst compounds is from 0.1:1 to 100:1, preferably from 0.25:1 to 75:1, preferably from 0.25:1 to 50:1, preferably from 0.5:1 to 30:1, preferably from 0.75:1 to 20:1, preferably from 0.8:1 to 10:1, preferably from 0.8:1 to 5:1, preferably from 0.8:1 to 2:1. In an embodiment, the molar ratio of Cr to Zr is 5:6.

Catalyst compounds represented by Formula I that are particularly useful in this invention include one or more of: ethylene (cyclopentadienyl)(pyrrolidine)chromium dichloride; dimethylsilyl (cyclopentadienyl)(pyrrolidine)chromium dichloride; phenylene (cyclopentadienyl)(pyrrolidine) chromium dichloride; and diphenylsilyl (cyclopentadienyl) (pyrrolidine)chromium dichloride.

Catalyst compounds represented by Formula II that are particularly useful in this invention include bis(1-methyl, 3-n-butyl cyclopentadienyl)zirconium dichloride.

When two transition metal compound based catalysts are used in one reactor as a mixed catalyst system, the two transition metal compounds are preferably chosen such that the two are compatible. A simple screening method such as by ^1H or ^{13}C NMR, known to those of ordinary skill in the art, can be used to determine which transition metal compounds are compatible. In a useful embodiment, compatible catalysts are capable of simultaneously making different polyethylene copolymers. Evidence of two different copolymers is shown in the GPC data from polymer samples derived from the mixed catalyst. In the case of Example 1, it is seen that a bimodal distribution arises from the mixed catalyst system of two catalysts that yield very different molecular weight distributions. FIG. **1** shows the GPC trace from the mixed catalyst system with the GPC trace from ethylene (cyclopentadienyl)(pyrrolidine)chromium dichloride alone overlaid. It is apparent that the higher molecular weight feature of the bimodal distribution of the mixed catalyst system derives from ethylene (cyclopentadienyl) (pyrrolidine)chromium dichloride. Thus, it is evident that the two catalysts are compatible and capable of simultaneously making polyethylene copolymer resins. It is preferable to use the same activator for the transition metal compounds, however, two different activators, such as a non-coordinating anion activator and an alumoxane, can be used in combination. If one or more transition metal compounds contain an X ligand which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane is typically contacted with the transition metal compounds prior to addition of the non-coordinating anion activator.

Methods to Prepare the Catalyst Compounds

Useful catalyst compounds represented by Formula I can be prepared by means known in the art, such as those described in DE 19710615; WO 2012/040147; and US 2013/225820. For example, ethylene(cyclopentadienyl) (pyrrolidine)chromium dichloride may be prepared by the method described in *J. Organometalics* 2000, 19, 388-402 (Dohring, A. et al.).

Useful catalyst compounds represented by Formula II can be prepared by means known in the art, such as those described in *Catalysis Letters* 2004, 98, 117-121. For example, bis(1-methyl, 3-n-butyl cyclopentadienyl)zirconium dichloride may be purchased from Boulder Scientific.

Activators

The terms "cocatalyst" and "activator" are used herein interchangeably and are defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst compound cation. Non-limiting activators, for example, include alumoxanes, aluminum alkyls, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. Preferred activators typically include alumoxane compounds, modified alumoxane compounds, and ionizing anion precursor compounds that abstract a reactive, σ-bound, metal ligand making the metal complex cationic and providing a charge-balancing noncoordinating or weakly coordinating anion.

In one embodiment, alumoxane activators are utilized as an activator in the catalyst composition. Alumoxanes are generally oligomeric compounds containing —$Al(R^1)$—O— sub-units, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. A useful alumoxane is a modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under U.S. Pat. No. 5,041,584).

When the activator is an alumoxane (modified or unmodified), some embodiments select the maximum amount of activator typically at up to a 5000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). The minimum activator-to-catalyst-compound is a 1:1 molar ratio. Alternate preferred ranges include from 1:1 to 500:1, alternately from 1:1 to 200:1, alternately from 1:1 to 100:1, or alternately from 1:1 to 50:1.

In an alternate embodiment, little or no alumoxane is used in the polymerization processes described herein. Preferably, alumoxane is present at zero mole %, alternately the alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1.

The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to a cation or which is only weakly coordinated to a cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with this invention are those that are compatible, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization.

It is within the scope of this invention to use an ionizing or stoichiometric activator, neutral or ionic, such as tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate, a tris perfluorophenyl boron metalloid precursor or a tris perfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Pat. No. 5,942,459), or combination thereof. It is also within the scope of this invention to use neutral or ionic activators alone or in combination with alumoxane or modified alumoxane activators.

Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium, and indium, or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogens, substituted alkyls, aryls, arylhalides, alkoxy, and halides. Preferably, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds, and mixtures thereof; preferred are alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls). More preferably, the three groups are alkyls having 1 to 4 carbon groups, phenyl, naphthyl, or mixtures thereof. Even more preferably, the three groups are halogenated, preferably fluorinated, aryl groups. A preferred neutral stoichiometric activator is tris perfluorophenyl boron or tris perfluoronaphthyl boron.

Ionic stoichiometric activator compounds may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP 0 570 982; EP 0 520 732; EP 0 495 375; EP 0 500 944; EP 0 277 003; EP 0 277 004; U.S. Pat. No. 5,153,157; U.S. Pat. No. 5,198,401; U.S. Pat. No. 5,066,741; U.S. Pat. No. 5,206,197; U.S. Pat. No. 5,241,025; U.S. Pat. No. 5,384,299; U.S. Pat. No. 5,502,124; and U.S. Ser. No. 08/285,380, filed Aug. 3, 1994; all of which are herein fully incorporated by reference.

Preferred compounds useful as an activator in the process of this invention comprise a cation, which is preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases, such as ethers, amines, and the like. Two classes of useful compatible non-coordinating anions have been disclosed in EP 0 277 003 A1, and EP 0 277 004 A1: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core; and 2) anions comprising a plurality of boron atoms such as carboranes, metallacarboranes, and boranes.

In a preferred embodiment, the stoichiometric activators include a cation and an anion component, and are preferably represented by the following formula (II):

$$(Z)_d^+(A^{d-}) \qquad \text{(II)}$$

wherein Z is (L-H) or a reducible Lewis Acid, L is an neutral Lewis base; H is hydrogen; $(L\text{-}H)^+$ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d−; and d is an integer from 1 to 3.

When Z is (L-H) such that the cation component is $(L\text{-}H)_d^+$, the cation component may include Bronsted acids such as protonated Lewis bases capable of protonating a moiety, such as an alkyl or aryl, from the bulky ligand metallocene containing transition metal catalyst precursor, resulting in a cationic transition metal species. Preferably, the activating cation $(L\text{-}H)_d^+$ is a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers, such as dimethyl ether diethyl ether, tetrahydrofuran, and dioxane, sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene, and mixtures thereof.

When Z is a reducible Lewis acid, it is preferably represented by the formula: (Ar_3C^+), where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C1 to C40 hydrocarbyl, preferably the reducible Lewis acid is represented by the formula: (Ph_3C^+), where Ph is phenyl or phenyl substituted with a heteroatom, a C_1 to

C_{40} hydrocarbyl, or a substituted C1 to C40 hydrocarbyl. In a preferred embodiment, the reducible Lewis acid is triphenyl carbenium.

The anion component A^{d-} includes those having the formula $[M^{k+}Q_n]^{d-}$ wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6, preferably 3, 4, 5, or 6; n−k=d; M is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than one occurrence is Q a halide, and two Q groups may form a ring structure. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} components also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

In a preferred embodiment, this invention relates to a method to polymerize olefins comprising contacting olefins (preferably ethylene and or propylene) with the catalyst compound and a boron containing NCA activator represented by the formula (14):

$$Z_d^+(A^{d-}) \qquad (14)$$

where: Z is (L-H) or a reducible Lewis acid; L is an neutral Lewis base (as further described above); H is hydrogen; (L-H) is a Bronsted acid (as further described above); A^{d-} is a boron containing non-coordinating anion having the charge d^- (as further described above); d^- is 1, 2, or 3.

In a preferred embodiment in any NCA's represented by Formula 14 described above, the reducible Lewis acid is represented by the formula: (Ar_3C^+), where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C1 to C40 hydrocarbyl, preferably the reducible Lewis acid is represented by the formula: (Ph_3C^+), where Ph is phenyl or phenyl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C1 to C40 hydrocarbyl.

In a preferred embodiment in any of the NCA's represented by Formula 14 described above, Z_d^+ is represented by the formula: $(L\text{-}H)_d^+$, wherein L is an neutral Lewis base; H is hydrogen; (L-H) is a Bronsted acid; and d is 1, 2, or 3, preferably $(L\text{-}H)_d^+$ is a Bronsted acid selected from ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof.

In a preferred embodiment in any of the NCA's represented by Formula 14 described above, the anion component A^{d-} is represented by the formula $[B^{k*+}Q^*_{n*}]^{d*-}$ wherein k* is 1, 2, or 3; n* is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4); n*−k*=d*; B is boron; and Q* is independently selected from hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q* having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q* a halide.

This invention also relates to a method to polymerize olefins comprising contacting olefins (such as ethylene and or propylene) with the catalyst compound, an optional chain transfer agent and an NCA activator represented by the formula (I):

$$R_nM^{**}(ArNHal)_{4-n} \qquad (I)$$

where R is a monoanionic ligand; M** is a Group 13 metal or metalloid; ArNHal is a halogenated, nitrogen-containing aromatic ring, polycyclic aromatic ring, or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together; and n is 0, 1, 2, or 3. Typically the NCA comprising an anion of Formula I also comprises a suitable cation that is essentially non-interfering with the ionic catalyst complexes formed with the transition metal compounds, preferably the cation is Z_d^+ as described above.

In a preferred embodiment in any of the NCA's comprising an anion represented by Formula I described above, R is selected from the group consisting of substituted or unsubstituted C_1 to C_{30} hydrocarbyl aliphatic or aromatic groups, where substituted means that at least one hydrogen on a carbon atom is replaced with a hydrocarbyl, halide, halocarbyl, hydrocarbyl or halocarbyl substituted organometalloid, dialkylamido, alkoxy, aryloxy, alkysulfido, arylsulfido, alkylphosphido, arylphosphide, or other anionic substituent; fluoride; bulky alkoxides, where bulky means C_4 to C_{20} hydrocarbyl groups; $—SR^1$, $—NR^2_2$, and $—PR^3_2$, where each R^1, R^2, or R^3 is independently a substituted or unsubstituted hydrocarbyl as defined above; or a C_1 to C_{30} hydrocarbyl substituted organometalloid.

In a preferred embodiment in any of the NCA's comprising an anion represented by Formula I described above, the NCA also comprises cation comprising a reducible Lewis acid represented by the formula: (Ar_3C^+), where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C1 to C40 hydrocarbyl, preferably the reducible Lewis acid represented by the formula: (Ph_3C^+), where Ph is phenyl or phenyl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl.

In a preferred embodiment in any of the NCA's comprising an anion represented by Formula I described above, the NCA also comprises a cation represented by the formula, $(L\text{-}H)_d^+$, wherein L is an neutral Lewis base; H is hydrogen; (L-H) is a Bronsted acid; and d is 1, 2, or 3, preferably $(L\text{-}H)_d^+$ is a Bronsted acid selected from ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof.

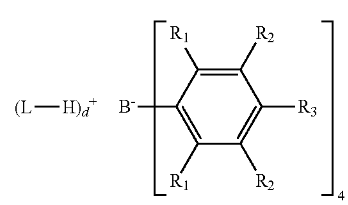
Further examples of useful activators include those disclosed in U.S. Pat. No. 7,297,653 and U.S. Pat. No. 7,799,879.

Another activator useful herein comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula (16):

$$(OX^{e+})_d(A^{d-})_e \qquad (16)$$

wherein OX^{e+} is a cationic oxidizing agent having a charge of e+; e is 1, 2, or 3; d is 1, 2, or 3; and A^{d-} is a non-coordinating anion having the charge of d− (as further described above). Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+, or Pb^{+2}. Preferred embodiments of A^{d-} include tetrakis (pentafluorophenyl)borate.

In another embodiment, the amidinate catalyst compounds and optional CTA's described herein can be used with Bulky activators. A "Bulky activator" as used herein refers to anionic activators represented by the formula:



where:

each R_1 is, independently, a halide, preferably a fluoride;

each R_2 is, independently, a halide, a C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula

—O—Si—R_a, where R_a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group (preferably R_2 is a fluoride or a perfluorinated phenyl group); each R_3 is a halide, C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula —O—Si—R_a, where R_a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group (preferably R_3 is a fluoride or a C_6 perfluorinated aromatic hydrocarbyl group); wherein R_2 and R_3 can form one or more saturated or unsaturated, substituted or unsubstituted rings (preferably R_2 and R_3 form a perfluorinated phenyl ring);

L is an neutral Lewis base; $(L-H)^+$ is a Bronsted acid; d is 1, 2, or 3;

wherein the anion has a molecular weight of greater than 1020 g/mol; and

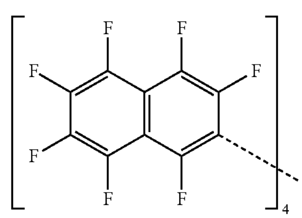
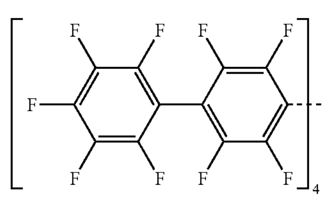
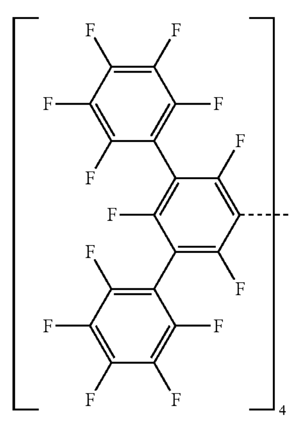
wherein at least three of the substituents on the B atom each have a molecular volume of greater than 250 cubic Å, alternately greater than 300 cubic Å, or alternately greater than 500 cubic Å.

"Molecular volume" is used herein as an approximation of spatial steric bulk of an activator molecule in solution. Comparison of substituents with differing molecular volumes allows the substituent with the smaller molecular volume to be considered "less bulky" in comparison to the substituent with the larger molecular volume. Conversely, a substituent with a larger molecular volume may be considered "more bulky" than a substituent with a smaller molecular volume.

Molecular volume may be calculated as reported in "A Simple "Back of the Envelope" Method for Estimating the Densities and Molecular Volumes of Liquids and Solids," Journal of Chemical Education, Vol. 71, No. 11, November 1994, pp. 962-964. Molecular volume (MV), in units of cubic Å, is calculated using the formula: $MV=8.3V_s$, where V_s is the scaled volume. V_s is the sum of the relative volumes of the constituent atoms, and is calculated from the molecular formula of the substituent using the following table of relative volumes. For fused rings, the V_s is decreased by 7.5% per fused ring.

Element	Relative Volume
H	1
1st short period, Li to F	2
2nd short period, Na to Cl	4
1st long period, K to Br	5
2nd long period, Rb to I	7.5
3rd long period, Cs to Bi	9

Exemplary bulky substituents of activators suitable herein and their respective scaled volumes and molecular volumes are shown in the table below. The dashed bonds indicate binding to boron, as in the general formula above.

Activator	Structure of boron substituents	Molecular Formula of each substituent	V_s	MV Per subst. (Å^3)	Total MV (Å^3)
Dimethylanilinium tetrakis(perfluoronaphthyl)borate		$C_{10}F_7$	34	261	1044
Dimethylanilinium tetrakis(perfluorobiphenyl)borate		$C_{12}F_9$	42	349	1396
[4-tButyl-$PhNMe_2H$] [$(C_6F_3(C_6F_5)_2)_4B$]		$C_{18}F_{13}$	62	515	2060

Exemplary bulky activators useful in catalyst systems herein include: trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl) borate, tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl) borate, tri(t-butyl)ammonium tetrakis(perfluoronaphthyl) borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl) borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl) borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis (perfluoronaphthyl)borate, tropillium tetrakis (perfluoronaphthyl)borate, triphenylcarbenium tetrakis (perfluoronaphthyl)borate, triphenylphosphonium tetrakis (perfluoronaphthyl)borate, triethylsilylium tetrakis (perfluoronaphthyl)borate, benzene(diazonium) tetrakis (perfluoronaphthyl)borate, trimethylammonium tetrakis (perfluorobiphenyl)borate, triethylammonium tetrakis (perfluorobiphenyl)borate, tripropylammonium tetrakis (perfluorobiphenyl)borate, tri(n-butyl)ammonium tetrakis (perfluorobiphenyl)borate, tri(t-butyl)ammonium tetrakis (perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis (perfluorobiphenyl)borate, N,N-diethylanilinium tetrakis (perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, [4-t-butyl-$PhNMe_2H$] [$(C_6F_3(C_6F_5)_2)_4B$], and the types disclosed in U.S. Pat. No. 7,297,653.

Illustrative, but not limiting, examples of boron compounds which may be used as an activator in the processes of this invention are:

trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, tri(t-butyl) ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate, tropillium tetraphenylborate, triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate, trimethylammonium tetrakis(pentafluorophenyl) borate, triethylammonium tetrakis(pentafluorophenyl) borate, tripropylammonium tetrakis(pentafluorophenyl) borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate, tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, N,N-diethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis (pentafluorophenyl)borate, tropillium tetrakis (pentafluorophenyl)borate, triphenylcarbenium tetrakis (pentafluorophenyl)borate, triphenylphosphonium tetrakis (pentafluorophenyl)borate, triethylsilylium tetrakis (pentafluorophenyl)borate, benzene(diazonium) tetrakis (pentafluorophenyl)borate, trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate, dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl) borate, tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trimethylammonium tetrakis (perfluoronaphthyl)borate, triethylammonium tetrakis (perfluoronaphthyl)borate, tripropylammonium tetrakis (perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis (perfluoronaphthyl)borate, tri(t-butyl)ammonium tetrakis (perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis (perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis (perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate, trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis (perfluorobiphenyl)borate, tri(n-butyl)ammonium tetrakis (perfluorobiphenyl)borate, tri(t-butyl)ammonium tetrakis (perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis (perfluorobiphenyl)borate, N,N-diethylanilinium tetrakis (perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis (trifluoromethyl)phenyl)borate, tropillium tetrakis(3,5-bis (trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis (3,5-bis(trifluoromethyl)phenyl)borate,

triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylsilylium tetrakis(3,5-bis(trifluoromethyl) phenyl)borate, benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, and dialkyl ammonium salts, such as: di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, and dicyclohexylammonium tetrakis(pentafluorophenyl)borate; and additional tri-substituted phosphonium salts, such as tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis (pentafluorophenyl)borate.

Preferred activators include N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,

triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, $[Ph_3C^+][B(C_6F_5)_4^-]$, $[Me_3NH^+][B(C_6F_5)_4^-]$; 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium; and tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine.

In a preferred embodiment, the activator comprises a triaryl carbonium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, triphenylcarbenium tetrakis(perfluoronaphthyl) borate, triphenylcarbenium tetrakis(perfluorobiphenyl) borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl) phenyl)borate).

In another embodiment, the activator comprises one or more of trialkylammonium tetrakis(pentafluorophenyl)borate, N,N-dialkylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trialkylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dialkylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trialkylammonium tetrakis (perfluoronaphthyl)borate, N,N-dialkylanilinium tetrakis (perfluoronaphthyl)borate, trialkylammonium tetrakis (perfluorobiphenyl)borate, N,N-dialkylanilinium tetrakis (perfluorobiphenyl)borate, trialkylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl) phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, (where alkyl is methyl, ethyl, propyl, n-butyl, sec-butyl, or t-butyl).

In a preferred embodiment, any of the activators described herein may be mixed together before or after combination with the catalyst compound and/or CTA, preferably before being mixed with the catalyst compound and/or CTA.

In some embodiments, two NCA activators may be used in the polymerization and the molar ratio of the first NCA activator to the second NCA activator can be any ratio. In some embodiments, the molar ratio of the first NCA activator to the second NCA activator is 0.01:1 to 10,000:1, preferably 0.1:1 to 1000:1, preferably 1:1 to 100:1.

Further, the typical activator-to-catalyst ratio, e.g., all NCA activators-to-catalyst ratio is a 1:1 molar ratio. Alternate preferred ranges include from 0.1:1 to 100:1, alternately from 0.5:1 to 200:1, alternately from 1:1 to 500:1, alternately from 1:1 to 1000:1. A particularly useful range is from 0.5:1 to 10:1, preferably 1:1 to 5:1.

It is also within the scope of this invention that the catalyst compounds can be combined with combinations of alumoxanes and NCA's (see for example, U.S. Pat. No. 5,153,157, U.S. Pat. No. 5,453,410, EP 0 573 120 B1, WO 94/07928, and WO 95/14044 which discuss the use of an alumoxane in combination with an ionizing activator).

Useful chain transfer agents are typically alkylalumoxanes, a compound represented by the formula AlR_3, ZnR_2 (where each R is, independently, a C_1-C_8 aliphatic radical, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

Optional Scavengers or Co-Activators

In addition to these activator compounds, scavengers or co-activators may be used. Aluminum alkyl or organoaluminum compounds which may be utilized as scavengers or co-activators include, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, and diethyl zinc.

Optional Support Materials

In embodiments herein, the catalyst system may comprise an inert support material. Preferably, the supported material is a porous support material, for example, talc and inorganic oxides. Other support materials include zeolites, clays, organoclays, or any other organic or inorganic support material and the like, or mixtures thereof.

Preferably, the support material is an inorganic oxide in a finely divided form. Suitable inorganic oxide materials for use in metallocene catalyst systems herein include Groups 2, 4, 13, and 14 metal oxides, such as silica, alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins, such as finely divided polyethylene. Particularly useful supports include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania, and the like. Preferred support materials include Al_2O_3, ZrO_2, SiO_2, and combinations thereof, more preferably SiO_2, Al_2O_3, or SiO_2/Al_2O_3.

It is preferred that the support material, most preferably an inorganic oxide, has a surface area in the range of from about 10 to about 700 m^2/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 μm. More preferably, the surface area of the support material is from about 50 to about 500 m^2/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 μm. Most preferably the surface area of the support material is in the range is from about 100 to about 400 m^2/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 5 to about 100 μm. The average pore size of the support material useful in the invention is in the range of from 10 to 1000 Å, preferably 50 to about 500 Å, and most preferably 75 to about 350 Å. In some embodiments, the support material is a high surface area, amorphous silica (surface area=300 m^2/gm; pore volume of 1.65 cm^3/gm). Preferred silicas are marketed under the tradenames of DAVISON 952 or DAVISON 955 by the Davison Chemical Division of W.R. Grace and Company. In other embodiments, DAVISON 948 is used.

The support material should be dry, that is, free of absorbed water. Drying of the support material can be effected by heating or calcining at about 100° C. to about 1000° C., preferably at least about 600° C. When the support material is silica, it is heated to at least 200° C., preferably about 200° C. to about 850° C., and most preferably at about 600° C.; and for a time of about 1 minute to about 100 hours, from about 12 hours to about 72 hours, or from about 24 hours to about 60 hours. The calcined support material must have at least some reactive hydroxyl (OH) groups to produce supported catalyst systems of this invention. The calcined support material is then contacted with at least one polymerization catalyst comprising at least one metallocene compound and an activator.

The support material, having reactive surface groups, typically hydroxyl groups, is slurried in a non-polar solvent and the resulting slurry is contacted with a solution of a metallocene compound and an activator. In some embodiments, the slurry of the support material is first contacted with the activator for a period of time in the range of from about 0.5 hours to about 24 hours, from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours. The solution of the metallocene compound is then contacted with the isolated support/activator. In some embodiments, the supported catalyst system is generated in situ. In alternate embodiment, the slurry of the support material is first contacted with the catalyst compound for a period of time in the range of from about 0.5 hours to about 24 hours, from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours. The slurry of the supported metallocene compound is then contacted with the activator solution.

The mixture of the metallocene, activator and support is heated to about 0° C. to about 70° C., preferably to about 23° C. to about 60° C., preferably at room temperature. Contact times typically range from about 0.5 hours to about 24 hours, from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours.

Suitable non-polar solvents are materials in which all of the reactants used herein, i.e., the activator, and the metallocene compound, are at least partially soluble and which are liquid at reaction temperatures. Preferred non-polar solvents are alkanes, such as isopentane, hexane, n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such as benzene, toluene, and ethylbenzene, may also be employed.

In a useful embodiment of the invention, the catalyst compounds are introduced to the support sequentially before or after contacting with activator. For example, the chromocene (such as those represented by Formula (I) above) may be contacted with the support, thereafter the support is contacted with the zirconocene or hafnocene (such as those represented by the Formula (II)). Activator may be contacted with the catalyst compounds before or after contacting with the support. In an alternate embodiment, the catalyst compounds (represented by Formula (I) and (II)) are not contacted with each other prior to contacting with the support.

Polymerization Processes

In embodiments herein, the invention relates to polymerization processes where monomer (such as propylene), and optionally comonomer, are contacted with a catalyst compound as described above and an activator. The catalyst compound and activator may be combined in any order, and are combined typically prior to contacting with the monomer.

Monomers useful herein include substituted or unsubstituted C2 to C40 alpha olefins, preferably C2 to C20 alpha olefins, preferably C2 to C12 alpha olefins, preferably ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In a preferred embodiment of the invention, the monomer comprises propylene and an optional comonomers comprising one or more ethylene or C_4 to C_{40} olefins, preferably C_4 to C_{20} olefins, or preferably C_6 to C_{12} olefins. The C_4 to C_{40} olefin monomers may be linear, branched, or cyclic. The C_4 to C_{40} cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups. In another preferred embodiment, the monomer comprises ethylene and an optional comonomers comprising one or more C_3 to C_{40} olefins, preferably C_4 to C_{20} olefins, or preferably C_6 to C_{12} olefins. The C_3 to C_{40} olefin monomers may be linear, branched, or cyclic. The C_3 to C_{40} cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups.

Exemplary C_2 to C_{40} olefin monomers and optional comonomers include ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, preferably hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives, preferably norbornene, norbornadiene, and dicyclopentadiene.

In a preferred embodiment, one or more dienes are present in the polymer produced herein at up to 10 wt %, preferably at 0.00001 to 1.0 wt %, preferably 0.002 to 0.5 wt %, even more preferably 0.003 to 0.2 wt %, based upon the total weight of the composition. In some embodiments, 500 ppm or less of diene is added to the polymerization, preferably 400 ppm or less, or preferably 300 ppm or less. In other embodiments, at least 50 ppm of diene is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

Preferred diolefin monomers useful in this invention include any hydrocarbon structure, preferably C_4 to C_{30}, having at least two unsaturated bonds, wherein at least two of the unsaturated bonds are readily incorporated into a polymer by either a stereospecific or a non-stereospecific catalyst(s). It is further preferred that the diolefin monomers be selected from alpha, omega-diene monomers (i.e., di-vinyl monomers). More preferably, the diolefin monomers are linear di-vinyl monomers, most preferably those containing from 4 to 30 carbon atoms. Examples of preferred dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (Mw less than 1000 g/mol). Preferred cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

Polymerization processes of this invention can be carried out in any manner known in the art. Any suspension, homogeneous, bulk, solution, slurry, or gas phase polymerization process known in the art can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Homogeneous polymerization processes and slurry processes are preferred. (A homogeneous polymerization process is defined to be a process where at least 90 wt % of the product is soluble in the reaction media.) A bulk homogeneous process is particularly preferred. (A bulk process is defined to be a process where monomer concentration in all feeds to the reactor is 70 volume % or more.) Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene). In another embodiment, the process is a slurry process. As used herein, the term "slurry polymerization process" means a polymerization process where a supported catalyst is employed and monomers are polymerized on the supported catalyst particles. At least 95 wt % of polymer products derived from the supported catalyst are in granular form as solid particles (not dissolved in the diluent).

Suitable diluents/solvents for polymerization include non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, such as can be found commercially (Isopar™); perhalogenated hydrocarbons, such as perfluorinated C_{4-10} alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In a preferred embodiment, aliphatic hydrocarbon solvents are used as the solvent, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof. In another embodiment, the solvent is not aromatic, preferably aromatics are present in the solvent at less than 1 wt %, preferably less than 0.5 wt %, preferably less than 0 wt % based upon the weight of the solvents.

In a preferred embodiment, the feed concentration of the monomers and comonomers for the polymerization is 60 vol % solvent or less, preferably 40 vol % or less, or preferably 20 vol % or less, based on the total volume of the feedstream. Conveniently, the polymerization may be run in a bulk process.

Preferred polymerizations can be run at any temperature and/or pressure suitable to obtain the desired ethylene polymers. Typical temperatures and/or pressures include a temperature in the range of from about 0° C. to about 300° C., preferably about 20° C. to about 200° C., preferably about 35° C. to about 150° C., preferably from about 40° C. to about 120° C., preferably from about 45° C. to about 80° C.; and at a pressure in the range of from about 0.35 MPa to about 10 MPa, preferably from about 0.45 MPa to about 6 MPa, or preferably from about 0.5 MPa to about 4 MPa.

In a typical polymerization, the run time of the reaction is up to 300 minutes, preferably in the range of from about 5 to 250 minutes, or preferably from about 10 to 120 minutes.

In a some embodiments, hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa), preferably from 0.01 to 25 psig (0.07 to 172 kPa), more preferably 0.1 to 10 psig (0.7 to 70 kPa).

In a some embodiments, ethylene is present in the polymerization reactor at a partial pressure of less than 4,000 kPa (preferably from 100 to 3,500 kPa, preferably from 500 to 3,000 kPa), more preferably from 500 to 2,000 kPa).

In an alternate embodiment, the activity of the catalyst system is at least 50 g/mmol/hour, preferably 500 or more g/mmol/hour, preferably 5000 or more g/mmol/hr, preferably 50,000 or more g/mmol/hr. In an alternate embodiment, the conversion of olefin monomer is at least 10%, based upon polymer yield and the weight of the monomer entering the reaction zone, preferably 20% or more, preferably 30% or more, preferably 50% or more, preferably 80% or more.

In a preferred embodiment, little or no alumoxane is used in the process to produce the polymers. Preferably, alumoxane is present at zero mol %, alternately the alumoxane is present at a molar ratio of aluminum to transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1.

In a preferred embodiment, little or no scavenger is used in the process to produce the ethylene polymer. Preferably, scavenger (such as tri alkyl aluminum) is present at zero mol %, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 15:1, preferably less than 10:1.

In a preferred embodiment, the polymerization: 1) is conducted at temperatures of 0 to 300° C. (preferably 25 to 150° C., preferably 40 to 120° C., preferably 45 to 80° C.); 2) is conducted at a pressure of atmospheric pressure to 10 MPa (preferably 0.35 to 10 MPa, preferably from 0.45 to 6 MPa, preferably from 0.5 to 4 MPa); 3) is conducted in an aliphatic hydrocarbon solvent (such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; preferably where aromatics are preferably present in the solvent at less than 1 wt %, preferably less than 0.5 wt %, preferably at 0 wt % based upon the weight of the solvents); 4) wherein the catalyst system used in the polymerization comprises less than 0.5 mol %, preferably 0 mol % alumoxane, alternately the alumoxane is present at a molar ratio of aluminum to transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1; 5) the polymerization preferably occurs in one reaction zone; 6) the productivity of the catalyst compound is at least 80,000 g/mmol/hr (preferably at least 150,000 g/mmol/hr, preferably at least 200,000 g/mmol/hr, preferably at least 250,000 g/mmol/hr, preferably at least 300,000 g/mmol/hr); 7) optionally scavengers (such as trialkyl aluminum compounds) are absent (e.g., present at zero mol %, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 15:1, preferably less than 10:1); and 8) optionally hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa) (preferably from 0.01 to 25 psig (0.07 to 172 kPa), more preferably 0.1 to 10 psig (0.7 to 70 kPa)). In a preferred embodiment, the catalyst system used in the polymerization comprises no more than one catalyst compound. A "reaction zone" also referred to as a "polymerization zone" is a vessel where polymerization takes place, for example, a batch reactor. When multiple reactors are used in either series or parallel configuration, each reactor is considered as a separate polymerization zone. For a multi-stage polymerization in both a batch reactor and a continuous reactor, each polymerization stage is considered as a separate polymerization zone. In a preferred embodiment, the polymerization occurs in one reaction zone. Room temperature is 23° C. unless otherwise noted.

Other additives may also be used in the polymerization, as desired, such as one or more scavengers, promoters, modifiers, chain transfer agents (such as diethyl zinc), reducing agents, oxidizing agents, hydrogen, aluminum alkyls, or silanes.

Useful chain transfer agents are typically alkylalumoxanes, a compound represented by the formula AlR_3, ZnR_2 (where each R is, independently, a C_1-C_8 aliphatic radical, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

Polyolefin Products

This invention also relates to compositions of matter produced by the methods described herein.

Likewise, the process of this invention produces olefin polymers, preferably polyethylene and polypropylene homopolymers and copolymers. In a preferred embodiment, the polymers produced herein are homopolymers of ethylene or are copolymers of ethylene preferably having from 0 to 25 mole % (alternately from 0.5 to 20 mole %, alternately from 1 to 15 mole %, preferably from 3 to 10 mole %) of one or more C_3 to C_{20} olefin comonomer (preferably C_3 to C_{12} alpha-olefin, preferably propylene, butene, hexene, octene, decene, dodecene, preferably propylene, butene, hexene, octene), or are copolymers of propylene preferably having from 0 to 25 mole % (alternately from 0.5 to 20 mole %, alternately from 1 to 15 mole %, preferably from 3 to 10 mole %) of one or more of C_2 or C_4 to C_{20} olefin comonomer (preferably ethylene or C_4 to C_{12} alpha-olefin, preferably ethylene, butene, hexene, octene, decene, dodecene, preferably ethylene, butene, hexene, octene).

In a preferred embodiment, the monomer is ethylene and the comonomer is hexene, preferably from 1 to 15 mole % hexene, alternately 1 to 10 mole %.

Typically, the polymers produced herein have an Mw of 5,000 to 3,000,000 g/mol (preferably 25,000 to 2,000,000 g/mol, preferably 50,000 to 1,500,000 g/mol, preferably 500,000 to 1,000,000 g/mol).

Typically, the polymers produced herein have an Mw/Mn of greater than 1 to 40 (alternately 1.2 to 20, alternately 1.3 to 10, alternately 1.4 to 5, alternately 1.5 to 4, alternately 1.5 to 3, alternately from 1 to 10, alternately from 1 to less than 8.0, alternately 1 to 7.5, alternately 1 to 7.0, alternately 1 to 6).

In a preferred embodiment of the invention, the polymer produced herein has a multimodal molecular weight distribution as determined by Gel Permeation Chromotography (GPC). In a preferred embodiment of the invention, the polymer produced herein does not have a unimodal molecular weight distribution as determined by Gel Permeation Chromotography (GPC). By "unimodal" is meant that the GPC trace has one peak or inflection point. By "multimodal" is meant that the GPC trace has at least two peaks or inflection points. An inflection point is that point where the second derivative of the curve changes in sign (e.g., from negative to positive or vice versus). Typically, the polymers produced herein have a bimodal molecular weight distribution.

Typically, the polymers produced herein have an Mw of 5,000 to 3,000,000 g/mol (preferably 25,000 to 2,000,000 g/mol, preferably 50,000 to 1,500,000 g/mol, preferably 500,000 to 1,000,000 g/mol) and have an Mw/Mn of greater than 1 to 10, alternately from 1 to less than 8.0, alternately from 1 to 7.5, alternately from 1 to 7.0, alternately from 1 to 6, alternately 1.2 to 5, alternately 1.5 to 4, alternately 1.5 to 3).

In some embodiments of the invention, the polymers produced herein have a bimodal Mw/Mn, an Mw of 5,000 to 3,000,000 g/mol (preferably 25,000 to 2,000,000 g/mol, preferably 50,000 to 1,500,000 g/mol, preferably 500,000 to 1,000,000 g/mol) and have an Mw/Mn of greater than 1 to 20, alternately from 1 to 10, alternately from 1 to less than 8.0, alternately from 1 to 7.5, alternately from 1 to 7.0, alternately from 1 to 6, alternately 1.2 to 5, alternately 1.5 to 4, alternately 1.5 to 3).

Unless otherwise indicated and for purposes of the claims to this invention Mw, Mn, MWD are determined by GPC as described in US 2006/0173123 pages 24-25, paragraphs [0334] to [0341].

In a preferred embodiment, the polymer produced herein has a composition distribution breadth index (CDBI) of 50% or more, preferably 60% or more, preferably 70% or more. CDBI is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published Feb. 18, 1993, specifically columns 7 and 8 as well as in Wild et al, J. Poly. Sci., Poly. Phys. Ed., Vol. 20, p. 441 (1982) and U.S. Pat. No. 5,008,204, including that fractions having a weight average molecular weight (Mw) below 15,000 are ignored when determining CDBI.

In a preferred embodiment, the polymer produced herein has a density (as determined by ASTM 1505) of less than 0.925 g/cc, preferably from 0.90 to 0.920 g/cc. Alternately, the polymer produced herein is an LDPE or an LLDPE.

Blends

In another embodiment, the polymer (preferably the polyethylene or polypropylene) produced herein is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate, LDPE, LLDPE, HDPE, ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidine fluoride, polyethylene glycols, and/or polyisobutylene.

In a preferred embodiment, the polymer (preferably the polyethylene or polypropylene) is present in the above blends, at from 10 to 99 wt %, based upon the weight of the polymers in the blend, preferably 20 to 95 wt %, even more preferably at least 30 to 90 wt %, even more preferably at least 40 to 90 wt %, even more preferably at least 50 to 90 wt %, even more preferably at least 60 to 90 wt %, even more preferably at least 70 to 90 wt %.

The blends described above may be produced by mixing the polymers of the invention with one or more polymers (as described above), by connecting reactors together in series to make reactor blends or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together prior to being put into the extruder or may be mixed in an extruder.

The blends may be formed using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process, which may include blending powders or pellets of the resins at the hopper of the film extruder. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX™ 1010 or IRGANOX™ 1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOS™ 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc; and the like.

Films

Any of the foregoing polymers may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and/or shrink films. These films may be formed by any number of well known extrusion or coextrusion techniques, such as a blown bubble film processing technique, wherein the composition can be extruded in a molten state through an annular die and then expanded to form a uni-axial or biaxial orientation melt prior to being cooled to form a tubular, blown film, which can then be axially slit and unfolded to form a flat film. Films may be subsequently unoriented, uniaxially oriented, or biaxially oriented to the same or different extents. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. The uniaxially orientation can be accomplished using typical cold drawing or hot drawing methods. Biaxial orientation can be accomplished using tenter frame equipment or double bubble processes and may occur before or after the individual layers are brought together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer or the polyethylene and polypropylene can be coextruded together into a film then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene, then optionally the combination could be oriented even further. Typically the films are oriented in the Machine Direction (MD) at a ratio of up to 15, preferably between 5 and 7, and in the Transverse Direction (TD) at a ratio of up to 15, preferably 7 to 9. However, in another embodiment the film is oriented to the same extent in both the MD and TD directions.

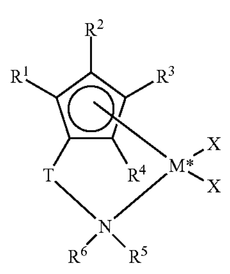
The films may vary in thickness depending on the intended application; however, films of a thickness from 1 to 50 μm are usually suitable. Films intended for packaging are usually from 10 to 50 μm thick. The thickness of the sealing layer is typically 0.2 to 50 μm. There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface.

In another embodiment, one or more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, flame treatment, or microwave. In a preferred embodiment, one or both of the surface layers is modified by corona treatment.

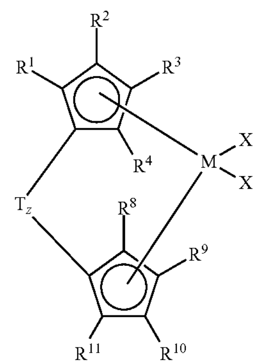
In another embodiment, this invention relates to:

1. A catalyst system comprising activator, support, catalyst compound represented by Formula I and catalyst compound represented by Formula II where:

Formula I is



and Formula II is



where

T is a bridging group; z is 0 or 1; N is nitrogen; M* is Cr, Mo, or W, where M* is in a +3 oxidation state prior to contacting with activator; each X, is independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, including that two X's may form a part of a fused ring or a ring system; each R^1, R^2, R^3, and R^4 is independently, hydrogen, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group; and each R^5 and R^6 is, independently, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group, where the R^5 and R^6 groups may form a fused ring or multicenter fused ring system where the rings may be aromatic, partially saturated or saturated;

M is Hf or Zr; and

each R^8, R^9, R^{10}, and R^{11} is, independently, hydrogen, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group.

2. The catalyst system of paragraph 1 wherein M* is Cr and M is Zr.

3. The catalyst system of paragraph 1 or 2 wherein the molar ratio of M* to M is 1:1000 to 1000:1.

4. The catalyst system of paragraph 1, 2, or 3 wherein the $N(R^5)(R^6)$ fragment is a neutral donor ligand.

5. The catalyst system of any of paragraphs 1 to 4 wherein the $N(R^5)(R^6)$ fragment is selected from the group consisting of pyrrolidine, aziridine, azetidine, piperidine, azepane, azocane, azonane, azecane, 1H-azirine, 1,2-dihydroazete, 2-pyrroline, 3-pyrroline, 1,4-dihydropyridine, azepine, azonine, indole, isoindole, indoline, isoindoline, and substituted analogs thereof, preferably where the substituent is one or more alkyl, aryl, silyl, or halide groups.

6. The catalyst system of any of paragraphs 1 to 5 wherein each R^5 and R^6, is, independently, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, docecyl, or an isomer thereof, or Cl, Br, F, I, or Si; and each R^1, R^2, R^3, R^4, R^8, R^9, R^{10}, and R^{11} is, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, docecyl, or an isomer thereof, Cl, Br, R, I, and Si.

7. The catalyst system of any of paragraphs 1 to 6 wherein each X is independently selected from chloride, bromide, methyl, ethyl, propyl, butyl, and pentyl.

8. The catalyst system of any of paragraphs 1 to 7 wherein T is represented by the formula, $(R^*_2G)_g$, where each G is C, Si, or Ge, g is 1 or 2, and each R* is, independently, hydrogen, halogen, C_1 to C_{20} hydrocarbyl or a C_1 to C_{20}

substituted hydrocarbyl, and two or more R* can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system.

9. The catalyst system of any of paragraphs 1 to 8, wherein the compound represented by Formula I comprises one or more of: ethylene (cyclopentadienyl)(pyrrolidine)chromium dichloride; dimethylsilyl (cyclopentadienyl)(pyrrolidine) chromium dichloride; phenylene (cyclopentadienyl)(pyrrolidine)chromium dichloride; and diphenylsilyl (cyclopentadienyl)(pyrrolidine)chromium dichloride; and the compound represented by Formula II comprises bis(1-methyl, 3-n-butyl cyclopentadienyl)zirconium dichloride.

10. The catalyst system of any of paragraphs 1 to 9, wherein the support is silica.

11. A process to polymerize olefins comprising contacting one or more olefins with the catalyst system of any of paragraphs 1 to 10.

12. The process of paragraph 11 wherein the activator comprises alumoxane.

13. The process of paragraph 11 or 12 wherein alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal of 10:1 or more, alternately 20:1 or more, alternately 100:1 or more.

14. The process of any of paragraphs 11 to 13 wherein the activator comprises a non-coordinating anion activator.

15. The process of any of paragraphs 11 to 14 wherein activator is represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein Z is (L-H) or a reducible Lewis Acid, L is an neutral Lewis base; H is hydrogen; $(L\text{-}H)^+$ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d−; and d is an integer from 1 to 3.

16. The process of any of paragraphs 11 to 14 wherein activator is represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein A^{d-} is a non-coordinating anion having the charge d−; d is an integer from 1 to 3, and Z is a reducible Lewis acid represented by the formula: (Ar_3C^+), where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl.

17. The process of any of paragraphs 11 to 14 wherein the activator is one or more of:

N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthyl)borate,
triethylammonium tetrakis(perfluoronaphthyl)borate,
tripropylammonium tetrakis(perfluoronaphthyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate,
tropillium tetrakis(perfluoronaphthyl)borate,
triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
triphenylphosphonium tetrakis(perfluoronaphthyl)borate,
triethylsilylium tetrakis(perfluoronaphthyl)borate,
benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
trimethylammonium tetrakis(perfluorobiphenyl)borate,
triethylammonium tetrakis(perfluorobiphenyl)borate,
tripropylammonium tetrakis(perfluorobiphenyl)borate,
tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate,
tropillium tetrakis(perfluorobiphenyl)borate,
triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
triphenylphosphonium tetrakis(perfluorobiphenyl)borate,
triethylsilylium tetrakis(perfluorobiphenyl)borate,
benzene(diazonium) tetrakis(perfluorobiphenyl)borate,
$[4\text{-t-butyl-PhNMe}_2H][(C_6F_3(C_6F_5)_2)_4B]$,
trimethylammonium tetraphenylborate,
triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate,
tropillium tetraphenylborate,
triphenylcarbenium tetraphenylborate,
triphenylphosphonium tetraphenylborate,
triethylsilylium tetraphenylborate,
benzene(diazonium)tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl)borate,
triethylammonium tetrakis(pentafluorophenyl)borate,
tripropylammonium tetrakis(pentafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate,
tropillium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
triphenylphosphonium tetrakis(pentafluorophenyl)borate,
triethylsilylium tetrakis(pentafluorophenyl)borate,
benzene(diazonium) tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl) borate,
dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl) borate,
N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl) borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate,
triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate,
tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,

tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
dicyclohexylammonium tetrakis(pentafluorophenyl)borate,
tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate,
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(perfluorophenyl)borate,
1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium,
tetrakis(pentafluorophenyl)borate,
4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine, and
triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

18. The process of any of paragraphs 11 to 17 wherein the process occurs at a temperature of from about 0° C. to about 300° C., at a pressure in the range of from about 0.35 MPa to about 10 MPa, and at a time up to 300 minutes.

19. The process of any of paragraphs 11 to 18 further comprising obtaining polymer.

20. The process of any of paragraphs 11 to 19 wherein the olefins comprise ethylene.

21. The process of any of paragraphs 11 to 18 further comprising obtaining ethylene polymer having an Mw from 50,000 to 3,000,000 g/mol, a bimodal molecular weight distribution, Mw/Mn, and an ethylene content of 80 to 100 mol %, and, optionally, an Mw/Mn of from 1 to 10.

EXPERIMENTAL

MAO is methyl alumoxane (30 wt % in toluene) obtained from Albemarle.

Examples

A solution of 30% wt. MAO in toluene (0.792 g; 4.09 mmol) was added to 1.5 mL of toluene; this solution was stirred for 15 min. To this solution was added 12 mg of ethylene (cyclopentadienyl)(pyrrolidine)chromium dichloride (0.041 mmol). This mixture was stirred for 20 min. To it was added 1.002 g of silica (Grace Davison 948, calcined at 600° C.). This mixture was then stirred by hand for 10 min, and dried in vacuo to yield the supported catalyst (Catalyst A). Separately, a solution of 2.2 mg (0.0051 mmol) of bis(1-methyl, 3-n-butyl cyclopentadienyl)zirconium dichloride in 1.5 mL of toluene was made. To this solution was added 193 mg of Catalyst A, which was washed in with 0.5 mL of toluene, and the mixture was stirred for 1 h. The mixture was filtered, and the solid so obtained was dried in vacuo to yield Catalyst A. The ratio of Cr to Zr on the support was 6:5.

Catalysts A and B were then both tested as described below and the resultant ethylene polymers yielded the GPC traces shown in FIG. 1. Catalyst A's PE had an Mw of approximately 2,700,000 g/mol whereas Catalyst B's PE had an Mw of about 1,000,000 g/mol.

Experimental—Polymerizations:

In the following experiments pressure is reported in atmospheres and pounds per square inch. The conversion factors to S.I. Units are; 1 psi equals 6.894757 kPa and 1 atm equals 101.325 kPa.

Transition metal compounds were supported as detailed in the examples above.

Solvents, polymerization grade toluene and hexanes were supplied by ExxonMobil Chemical Company and thoroughly dried and degassed prior to use.

Polymerization grade ethylene was used and further purified by passing it through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, Calif.) followed by a 500 cc column packed with dried 3 Å mole sieves purchased from Aldrich Chemical Company, and a 500 cc column packed with dried 5 Å mole sieves purchased from Aldrich Chemical Company.

TnOAl (tri-n-octylaluminum, neat) was used as a 2 mmol/L solution in toluene.

Reactor Description and Preparation: Polymerizations were conducted in an inert atmosphere (N_2) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor=22.5 mL), septum inlets, regulated supply of nitrogen, ethylene and propylene, and equipped with disposable PEEK mechanical stirrers (800 RPM). The autoclaves were prepared by purging with dry nitrogen prior to use.

Ethylene/1-hexene Copolymerization:

The reactor was prepared as described above, and then purged with ethylene. Isohexane,1-hexene and TnOAl were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (85° C.) and charged with ethylene to process pressure (130 psig=896 kPa) while stirring at 800 RPM. The transition metal compound "TMC" (100 μL of a 3 mg/mL toluene slurry, unless indicated otherwise) was added via syringe with the reactor at process conditions. TnOAl was used as 200 μL of a 20 mmol/L in isohexane solution. Amounts of reagents not specified above are given in Table 1. Ethylene was allowed to enter (through the use of computer controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (+/−2 psig). Reactor temperature was monitored and typically maintained within +/−1° C. Polymerizations were halted by addition of approximately 50 psi O_2/Ar (5 mole % O_2) gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added or for a maximum of 20 minutes polymerization time. The final conversion (in psi) of ethylene added/consumed is reported in Table 1, in addition to the quench time for each run. The reactors were cooled and vented. The polymer was isolated after the solvent was removed in-vacuo. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per atmosphere ethylene per hour of reaction time (g/mmol·hr·atm).

Polymer Characterization:

Polymer characterization results for polyethylene samples are reported in Table 2. For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-

Aldrich) containing 2,6-di-tert-butyl-4-methylphenol (BHT, 99% from Aldrich) at 160° C. in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution is between 0.4 to 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples are cooled to 135° C. for testing.

Molecular weights (weight average molecular weight (Mw) and number average molecular weight (Mn)) and molecular weight distribution (MWD=Mw/Mn), which is also sometimes referred to as the polydispersity (PDI) of the polymer, were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with evaporative light scattering detector and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 5000 and 3,390,000). Samples were run in TCB at (135° C. sample temperatures, 160° C. oven/columns) using three Polymer Laboratories: PLgel 10 μm Mixed-B 300×7.5 mm columns in series. No column spreading corrections were employed. Numerical analyses were performed using Epoch® software available from Symyx Technologies.

The sample preparation for SAMMS (Sensory Array Modular Measurement System) thermal analysis measurements involved depositing the stabilized polymer solution onto a silanized wafer (Part Number S10457, Symyx). The solvent was then evaporated off at ~145° C. By this method, approximately between 0.12 and 0.24 mg of polymer is deposited onto each corresponding wafer cell. Thermal analysis was measured on a Symyx Technologies SAMMS instrument that measures polymer melt temperatures via the 3 co technique. The analysis first employs a rapid-scan protocol that heats each cell from 27° C. to 200° C. in ~35 seconds and then rapidly cools the sample to room temperature. This complete procedure takes approximately 60 seconds per cell and is used to minimize each sample's thermal history. The second step involves running a high-resolution scan protocol to measure the second melt of the sample. The protocol heats each cell from 27° C. to 200° C. in ~3 minutes and then rapidly cools the sample to room temperature. The high-resolution scan takes approximately three times the amount of time to complete as the rapid-scan protocol. If multiple melting peaks are present, Epoch® Software reports the largest amplitude peak. SAMMS data is reported under the heading of Tm (° C.).

Samples for infrared analysis were prepared by depositing the stabilized polymer solution onto a silanized wafer (Part number S10860, Symyx). By this method, approximately between 0.12 and 0.24 mg of polymer is deposited on the wafer cell. The samples were subsequently analyzed on a Brucker Equinox 55 FTIR spectrometer equipped with Pikes's MappIR specular reflectance sample accessory. Spectra, covering a spectral range of 5000 cm^{-1} to 500 cm^{-1}, were collected at a 2 cm^{-1} resolution with 32 scans.

TABLE 1

Ethylene-hexene copolymerization Runs (data is an average of 2 runs)

Ex #	Catalyst	Catalyst	TnOAl	Total	1-hexene	Final	Quench	Polymer	Activity
PE-1	0.3	—	0.004	5	30	30.4	2700	0.0499	783
PE-2	0.3	—	0.004	5	115	23.4	2700	0.0414	650
PE-3	0.3	—	0.004	5	200	27.8	2700	0.0397	623
PE-4	—	0.3	0.004	5	30	55.1	1830	0.0861	571
PE-5	—	0.3	0.004	5	115	55.1	1230	0.0922	910
PE-6	—	0.3	0.004	5	200	55.1	1160	0.0928	971

TABLE 2

Ex #	TMC	Mw	Mn	Mw/Mn	Tm (° C.)	Wt % hexene
PE-1	—	2,864,000	1,315,000	2.3	125.6	5.7
PE-2	—	2,930,000	1,263,000	2.4	124.7	5.8
PE-3	—	2,577,000	920,000	2.9	123.8	6.7
PE-4	6:5	1,081,000	304,000	3.6	127.9	3.4
PE-5	6:5	1,035,000	289,000	3.6	121.5	5.2
PE-6	6:5	1,081,000	311,000	3.5	118.7	6.2

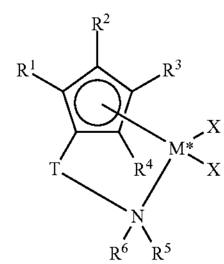
PE-1, PE-2, and PE-3 are chromocene catalyst only.

All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including." Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of", "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

The invention claimed is:

1. A catalyst system comprising activator, support, catalyst compound represented by Formula I and catalyst compound represented by Formula II where:

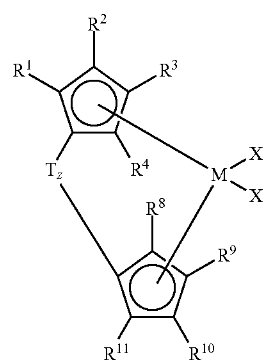
Formula I is



where

T is a bridging group; N is nitrogen; M* is Cr, Mo, or W, where M* is in a +3 oxidation state prior to contacting with activator; each X, is independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, two X's optionally form a part of a fused ring or a ring system; each R^1, R^2, R^3, and R^4 is independently, hydrogen, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group; and each R^5 and R^6 is, independently, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group, where the R^5 and R^6 groups optionally form a fused ring or multicenter fused ring system where the rings are aromatic, partially saturated or saturated; and

Formula II is:



where

M is Hf or Zr; z is 0 or 1; R^1, R^2, R^3, R^4, T and X, are as described above; and

each R^8, R^9, R^{10}, and R^{11} is, independently, hydrogen, a C_1 to C_{12} hydrocarbyl, a substituted C_1 to C_{12} hydrocarbyl, a heteroatom, or substituted heteroatom group.

2. The catalyst system of claim **1**, wherein M* is Cr and M is Zr.

3. The catalyst system of claim **1**, wherein the molar ratio of M* to M is 1:1000 to 1000:1.

4. The catalyst system of claim **1**, wherein the $N(R^5)(R^6)$ fragment is a neutral donor ligand.

5. The catalyst system of claim **1**, wherein the $N(R^5)(R^6)$ fragment is selected from the group consisting of pyrrolidine, aziridine, azetidine, piperidine, azepane, azocane, azonane, azecane, 1H-azirine, 1,2-dihydroazete, 2-pyrroline, 3-pyrroline, 1,4-dihydropyridine, azepine, azonine, indole, isoindole, indoline, isoindoline or a substituted analog thereof.

6. The catalyst system of claim **1**, wherein each R^5 and R^6, is, independently, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, docecyl, or an isomer thereof, or Cl, Br, F, I or Si; and each R^1, R^2, R^3, R^4, R^8, R^9, R^{10}, and R^{11} is, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, docecyl, or an isomer thereof, Cl, F, I, Br, and Si.

7. The catalyst system of claim **1**, wherein each X is independently selected from chloride, bromide, methyl, ethyl, propyl, butyl, and pentyl.

8. The catalyst system of claim **1**, wherein T is represented by the formula, $(R^*{}_2G)_g$, where each G is C, Si, or Ge, g is 1 or 2, and each R* is, independently, hydrogen, halogen, C_1 to C_{20} hydrocarbyl or a C_1 to C_{20} substituted hydrocarbyl, and two or more R* can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system.

9. The catalyst system of claim **1**, wherein the compound represented by Formula I comprises one or more of: ethylene (cyclopentadienyl)(pyrrolidine)chromium dichloride; dimethylsilyl (cyclopentadienyl)(pyrrolidine)chromium dichloride; phenylene (cyclopentadienyl)(pyrrolidine)chromium dichloride; and diphenylsilyl (cyclopentadienyl)(pyrrolidine)chromium dichloride; and the compound represented by Formula II comprises bis(1-methyl, 3-n-butyl cyclopentadienyl)zirconium dichloride.

10. The catalyst system of claim **1**, wherein the support is silica.

11. A process to polymerize olefins comprising contacting one or more olefins with the catalyst system of claim **1**.

12. The process of claim **11**, wherein the activator comprises alumoxane.

13. The process of claim **11**, wherein alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal of 100:1 or more.

14. The process of claim **11**, wherein the activator comprises a non-coordinating anion activator.

15. The process of claim **11**, wherein activator is represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein Z is (L-H) or a reducible Lewis Acid, L is an neutral Lewis base; H is hydrogen; $(L\text{-}H)^+$ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d−; and d is an integer from 1 to 3.

16. The process of claim **11**, wherein activator is represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein A^{d-} is a non-coordinating anion having the charge d−; d is an integer from 1 to 3, and Z is a reducible Lewis acid represented by the formula: (Ar_3C^+), where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl.

17. The process of claim **11**, wherein the activator is one or more of:

N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthyl)borate,
triethylammonium tetrakis(perfluoronaphthyl)borate,
tripropylammonium tetrakis(perfluoronaphthyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate,
tropillium tetrakis(perfluoronaphthyl)borate,
triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
triphenylphosphonium tetrakis(perfluoronaphthyl)borate,
triethylsilylium tetrakis(perfluoronaphthyl)borate,
benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
trimethylammonium tetrakis(perfluorobiphenyl)borate,
triethylammonium tetrakis(perfluorobiphenyl)borate,
tripropylammonium tetrakis(perfluorobiphenyl)borate,
tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,

N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate,
tropillium tetrakis(perfluorobiphenyl)borate,
triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
triphenylphosphonium tetrakis(perfluorobiphenyl)borate,
triethylsilylium tetrakis(perfluorobiphenyl)borate,
benzene(diazonium) tetrakis(perfluorobiphenyl)borate,
[4-t-butyl-PhNMe$_2$H][($C_6F_3(C_6F_5)_2)_4$B],
trimethylammonium tetraphenylborate,
triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate,
tropillium tetraphenylborate,
triphenylcarbenium tetraphenylborate,
triphenylphosphonium tetraphenylborate,
triethylsilylium tetraphenylborate,
benzene(diazonium)tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl)borate,
triethylammonium tetrakis(pentafluorophenyl)borate,
tripropylammonium tetrakis(pentafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate,
tropillium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
triphenylphosphonium tetrakis(pentafluorophenyl)borate,
triethylsilylium tetrakis(pentafluorophenyl)borate,
benzene(diazonium) tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate,
dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,

triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
dicyclohexylammonium tetrakis(pentafluorophenyl)borate,
tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate,
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(perfluorophenyl)borate,
1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium,
tetrakis(pentafluorophenyl)borate,
4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine, and
triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

18. The process of claim **11**, wherein the process occurs at a temperature of from about 0° C. to about 300° C., at a pressure in the range of from about 0.35 MPa to about 10 MPa, and at a time up to 300 minutes.

19. The process of claim **11** further comprising obtaining polymer.

20. The process of claim **11** wherein the olefins comprise ethylene.

21. The process of claim **11** further comprising obtaining ethylene polymer having an Mw from 50,000 to 3,000,000 g/mol, a bimodal molecular weight distribution, Mw/Mn, an ethylene content of 80 to 100 mol %.

22. The process of claim **11**, wherein z is 0.

23. The catalyst system of claim **1**, wherein z is 0.

24. The process of claim **11**, further comprising obtaining ethylene polymer having an Mw from 50,000 to 3,000,000 g/mol, a bimodal molecular weight distribution, Mw/Mn, an ethylene content of 80 to 100 mol %, and an Mw/Mn of from 1 to 10.

25. The process of claim **11**, further comprising obtaining ethylene polymer having an Mw from 50,000 to 3,000,000 g/mol, a bimodal molecular weight distribution, Mw/Mn, an ethylene content of 80 to 100 mol %, and an Mw/Mn of from 1 to less than 8.

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